

Assessing the behavior of typically lithophile elements under highly reducing conditions relevant to the planet Mercury

Rick Rowland II¹, Kathleen E. Vander Kaaden¹, Francis M. McCubbin², and Lisa R. Danielson¹

1-Jacobs Technology, JETS contract, NASA Johnson Space Center, 2101 NASA Parkway, Houston, TX 77058, USA

2-NASA Johnson Space Center, Mail Code XI2, 2102 NASA Parkway, Houston, TX 77058, USA

(Correspondance to Richard.L.Rowland@NASA.gov)

Introduction:

With the data returned from the MErcury Surface, Space ENvironment, GEochemistry, and Ranging (MESSENGER) mission, there are now numerous constraints on the physical and chemical properties of Mercury, including its surface composition (e.g., Evans et al. 2012; Nittler et al. 2011; Peplowski et al. 2012; Weider et al. 2012). The high S and low FeO contents observed from MESSENGER on the planet's surface suggests a low oxygen fugacity of the present planetary materials. Estimates of the oxygen fugacity for Mercurian magmas are approximately 3-7 log units below the Iron-Wüstite (Fe-FeO) oxygen buffer (McCubbin et al. 2012; Zolotov et al. 2013), several orders of magnitude more reducing than other terrestrial bodies we have data from such as the Earth, Moon, or Mars (Herd 2008; Sharp, McCubbin, and Shearer 2013; Wadhwa 2008). Most of our understanding of elemental partitioning behavior comes from observations made on terrestrial rocks, but Mercury's oxygen fugacity is far outside the conditions of those samples. With limited oxygen available, lithophile elements may instead exhibit chalcophile, halophile, or siderophile behaviors. Furthermore, very few natural samples of rocks that formed under reducing conditions are available in our collections (e.g., enstatite chondrites, achondrites, aubrites). The goal of this study is to conduct experiments at high pressure and temperature conditions to determine the elemental partitioning behavior of typically lithophile elements as a function of decreasing oxygen fugacity.

Methods:

Experiments were conducted at Johnson Space Center (JSC) at 1 GPa in a 13 mm QUICKpress piston cylinder, at temperatures up to 1700 °C, and at 4 GPa in an 880-ton multi-anvil press, at temperatures up to 1850 °C. The composition of starting materials for the experiments were selected for the final run products to contain metal, silicate melt, and sulfide melt phases. Oxygen fugacity is controlled in the experiments by adding silicon metal to the samples, using the Si-SiO₂ oxygen buffer, which is ~5 log units more reducing than the Fe-FeO oxygen buffer at our temperatures of interest. The target silicate melt composition is diopside (CaMgSi₂O₆) because measured surface compositions indicate partial melting of a pyroxene-rich mantle (e.g., Vander Kaaden and McCubbin, 2016). Variable time series experiments from <1 to 4 hours were completed to ensure the measurements reflect equilibrium conditions. Once the preliminary experiments have been completed, elements detected on Mercury's surface by MESSENGER (H, C, Na, Al, Cl, K, Ti, Cr, Mn, Fe) and other geochemically relevant elements (Li, N, F, P, Sc, Co, Ni, Zn, Ga, Ge, Se, Br, Rb, Sr, Y, Zr, Mo, Ag, Cd, In, Sn, Sb, I, Cs, Ba, La,

Ce, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu, Hf, Tl, Pb, Bi) will be added to the starting composition at trace abundances (~500 ppm) so that they are close enough to infinite dilution to follow Henry's law of trace elements, and their partitioning behavior can be measured between the metal, silicate, and sulfide phases using laser-ablation inductively coupled plasma mass spectrometry.

All run products were polished using hexagonal boron nitride as a lubricant instead of water or oil because it has been demonstrated that some cations (especially alkalis) are water and oil soluble when bonded to sulfide (Murthy et al. 2003). Backscattered electron imaging (for textural analysis) and EPMA of all phases was carried out using a JEOL 8530F electron microprobe, at JSC. All phases including silicate glass, metals, and sulfides, were analyzed. An accelerating voltage of 15 keV was used for all analyses. A beam current of 15 nA was used for silicate analyses, whereas metals and sulfides were analyzed using a beam current of 20 nA. A broad beam (10–20 μm) was used for glass analyses and a focused beam (1–5 μm) was used for the metals, and sulfides. Standards included diopside (for Si, Ca, Mg), troilite (S), olivine (Fe, Mg, Si), and various glass standards (Ca, Mg, Fe, Si) to analyze the silicate portion of the experimental charges. Metal and sulfide standards include Si metal, Fe-metal, diopside (Mg, Ca), and troilite (S). Peak positions were checked on the silicate standards used for metal and sulfide analyses and were compared to the peak positions in the experimental charge to ensure that analyses were conducted at the correct peak position. Peak count times ranged from 30–60 seconds and background count times ranged from 15–30 seconds, respectively.

Discussion:

After the analysis of the experimental charges, the weight percent ratios of the silicate, sulfide, and metal starting materials were varied to make sure that sulfur saturation in the silicate melts was reached and an Si-bearing metal phase was present at the end of each experiment. With the completion of this study, we will be able to show which elements are most likely to retain their lithophile character and hence be incorporated into the silicate portion of Mercury, which elements are likely contained within sulfide phases (chalcophile elements), and which elements prefer to be in the core of reducing planetary bodies (siderophile elements). Furthermore, the results of these experiments will allow us to assess the thermal and magmatic evolution of the planet Mercury from a geochemical standpoint.

References:

Evans, L. G., et al. 2012. 'Major-element abundances on the surface of Mercury: Results from the MESSENGER Gamma-Ray Spectrometer', *Journal of Geophysical Research-Planets*, 117: E00L07. Herd, C. D. K. 2008. 'Basalts as probes of planetary interior redox state', *Oxygen in the Solar System*, 68: 527-53. McCubbin, F. M., et al. 2012. 'Is Mercury a volatile-rich planet?', *Geophysical Research Letters*, 39. Murthy, V. M., et al. 2003. 'Experimental evidence that potassium is a substantial radioactive heat source in planetary cores', *Nature*, 423: 163-65. Nittler, L. R., et al. 2011. 'The Major-Element Composition of Mercury's Surface from MESSENGER X-ray Spectrometry', *Science*, 333: 1847-50. Peplowski, P. N., D. J. et al. 2012. 'Variations in the abundances of potassium and thorium on the surface of Mercury: Results from the MESSENGER Gamma-Ray Spectrometer', *Journal of Geophysical Research - Planets*, 117. Sharp, Z. D., et al. 2013. 'A hydrogen-based oxidation mechanism relevant to planetary formation', *Earth and*

Planetary Science Letters, 380: 88-97. Vander Kaaden, K. E., and F. M. McCubbin. 2016. 'The origin of boninites on Mercury: An experimental study of the northern volcanic plains lavas', *Geochimica Et Cosmochimica Acta*, 173: 246-63. Wadhwa, M. 2008. 'Redox conditions on small bodies, the Moon, and Mars', *Oxygen in the Solar System*, 68: 493-510. Weider, S. Z., et al. 2012. 'Chemical heterogeneity on Mercury's surface revealed by the MESSENGER X-Ray Spectrometer', *Journal of Geophysical Research - Planets*, 117. Zolotov, M. Y., et al. 2013. 'The redox state, FeO content, and origin of sulfur-rich magmas on Mercury', *Journal of Geophysical Research-Planets*, 118.